Applied Energy 114 (2014) 104–113

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass

Wei-Hsin Chen [a,*], Ke-Miao Lu [b], Wen-Jhy Lee [b,*], Shih-Hsien Liu [c], Ta-Chang Lin [b]

[a] *Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC*
[b] *Department of Environmental Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC*
[c] *Iron and Steel Research and Development Department, China Steel Corporation, Kaohsiung 812, Taiwan, ROC*

HIGHLIGHTS

- Non-oxidative and oxidative torrefaction of biomass is studied.
- Two fibrous biomasses and two ligneous biomasses are tested.
- SEM observations of four biomasses are provided.
- Fibrous biomass is more sensitive to O_2 concentration than ligneous biomass.
- The performance of non-oxidative torrefaction is better than that of oxidative torrefaction.

ARTICLE INFO

Article history:
Received 16 May 2013
Received in revised form 10 September 2013
Accepted 18 September 2013
Available online 15 October 2013

Keywords:
Non-oxidative and oxidative torrefaction
Fibrous and ligneous biomass
SEM observation
Energy-mass co-benefit index (EMCI)
Energy yield

ABSTRACT

Oxidative torrefaction is a method to reduce the operating cost of upgrading biomass. To understand the potential of oxidative torrefaction and its impact on the internal structure of biomass, non-oxidative and oxidative torrefaction of two fibrous biomass materials (oil palm fiber and coconut fiber) and two ligneous ones (eucalyptus and *Cryptomeria japonica*) at 300 °C for 1 h are studied and compared with each other. Scanning electron microscope (SEM) observations are also performed to explore the impact of torrefaction atmosphere on the lignocellulosic structure of biomass. The results indicate that the fibrous biomass is more sensitive to O_2 concentration than the ligneous biomass. In oxidative torrefaction, an increase in O_2 concentration decreases the solid yield. The energy yield is linearly proportional to the solid yield, which is opposite to the behavior of non-oxidative torrefaction. The performance of non-oxidative torrefaction is better than that of oxidative torrefaction. As a whole, ligneous biomass can be torrefied in oxidative environments at lower O_2 concentrations, whereas fibrous biomass is more suitable for non-oxidative torrefaction.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass energy or bioenergy is the largest and the most important renewable energy in the world and accounts for around 10% of primary energy consumption [1]. Biomass can be consumed alone or blended with coal for combustion [2], gasification [3], and pyrolysis [4,5]. However, the properties of raw biomass are obviously different from those of coal. For example, the fixed carbon (FC) and volatile matter (VM) of biomass (dry basis) are typically in the ranges of 0.5–20 wt.% and 67–88 wt.%, respectively [6]; whereas they are 46–92 wt.% and 0.9–50 wt.% in coal [7]. The contents of element carbon and oxygen in raw biomass range from approximately 39 to 50 wt.% and from 37 to 50 wt.%, respectively [7], and they are between 64 and 92 wt.% and 1 and 25 wt.% in coal, respectively [7]. Seeing that raw biomass has lower FC and element carbon, its higher heating value (HHV) is lower than that of coal. Specifically, the HHV of biomass and coal are in the ranges of approximately 15–20 MJ kg^{-1} [6] and 25–35 MJ kg^{-1} [7], respectively.

Biomass can be upgraded to become a better solid fuel via torrefaction in which biomass is thermally degraded in a non-oxidative environment at temperatures of 200–300 °C [8,9], namely, the non-oxidative torrefaction. Within this temperature range, the main constituents contained in biomass, namely, hemicellulose, cellulose, and lignin, will be thermally decomposed, especially for hemicellulose [10]. After undergoing torrefaction, the VM of biomass is decreased to 34–85 wt.%, whereas its FC is increased to 13–45 wt.% [11–14]. The elements carbon and oxygen in biomass are changed to 45–68 and 11–45 wt.%, respectively [13,15–17]. The solid yield of biomass from torrefaction is between

---

* Corresponding authors. Tel.: +886 6 2757575x63621; fax: +886 6 2389940 (W.H. Chen), tel.: +886 6 2757575x65831; fax: +886 6 2752790 (W.J. Lee).

E-mail addresses: weihsinchen@gmail.com (W.-H. Chen), wjlee@mail.ncku.edu.tw (W.-J. Lee).

0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.09.045

24 and 95 wt.% [6] and the HHV of torrefied biomass is between 16 and 29 MJ kg^{-1}. As a consequence, the energy yield is in the range of 29–98% [6], depending on the torrefaction temperature and duration [6,17–21]. The efficiencies of combustion [16], gasification [22], and pyrolysis [23,24] of torrefied biomass are higher than those of its parent material, but additional operating costs are required due to the supplies of heat and nitrogen for torrefaction. Therefore, the reduction of operating costs is an important issue to practice torrefaction commercially.

A reduction in cost could potentially be achieved if torrefaction is carried out in an oxidative atmosphere, namely, the oxidative torrefaction, because of the utilization of air and exothermic reactions involved in an oxidizing environment. Recently, a number of studies relating to oxidative torrefaction have been carried out. Wang et al. [25] torrefied sawdust using carrier gases containing 0, 3, and 6 vol.% of O_2 at 250, 270, and 290 °C followed by pelletization. They found that the properties of oxidatively torrefied sawdust and its pellets, such as density, energy consumption for pelletization, HHV, and energy yield, were close to those of non-oxidatively torrefied sawdust. Rousset et al. [26] investigated the physical and chemical properties of eucalyptus grandis which was torrefied in the atmospheres at O_2 concentrations of 2, 6, 10, and 21 vol.% and temperatures of 240 and 280 °C for 1 h. They pointed out that the O_2 concentration did not substantially affect the solid yield and composition of the torrefied biomass at 240 °C. The influence of increasing O_2 concentration on solid yield reduction and componential change at 280 °C was more than that at 240 °C, but it was significant only at the O_2 concentration of 21 vol.%. Lu et al. [13] evaluated the properties of oil palm fiber and eucalyptus pretreated in N_2 and air atmospheres (0 and 21 vol.% of O_2) at temperatures of 250–350 °C for 1 h. They found that oil palm fiber was feasible to be torrefied in a N_2 environment but inappropriate in air, as the results of low solid and energy yields. On the other hand, N_2 and air could be employed to upgrade eucalyptus at temperatures of 325 and 275 °C, respectively. Uemura et al. [27] explored the effects of varied temperature (220, 250, and 300 °C), oxygen concentration (0, 3, 9, and 15 vol.%), and biomass size (0.375, 1.5, 3, and 6 mm) on the solid and energy yields of oil palm empty fruit bunches (EFBs). They discovered that the solid yield decreased with increasing O_2 concentration and temperature; the energy yield also decreased with increasing O_2 concentration. However, the solid and energy yields were unaffected by biomass size. Chen et al. [28] performed biomass torrefaction in inert and oxidative environments at various superficial velocities. They found that thermal degradation of biomass in N_2 was controlled by internal heat and mass transfer. For biomass torrefied in air (or oxidative atmosphere), surface oxidation was the dominant mechanism in pretreating biomass.

The above research has provided some valuable information on biomass oxidative torrefaction. However, more detailed information for the operation of oxidative torrefaction is required. To provide a comprehensive insight into the operation of oxidative torrefaction, four types of biomass in various oxidative environments will be studied. Particular attention is paid to the property variations of the materials due to the operations. Moreover, detailed SEM images of biomass before and after torrefaction will be observed and discussed to figure out the impact of non-oxidative and oxidative torrefaction upon the lignocellulosic structure.

2. Experiment

2.1. Material

Four kinds of biomass, oil palm fiber (OPF), coconut fiber (CF), eucalyptus (EU), and *Cryptomeria japonica* (CJ), were selected as samples for investigation. The first two materials are fibrous biomass and the last two materials are ligneous biomass. The photographs and properties of the four untreated biomasses are listed in Table 1. OPF has the highest ash content (=7.03 wt.%) and the

Table 1
A list of properties of raw biomass.

Biomass	Oil palm fiber	Coconut fiber	Eucalyptus	*Cryptomeria japonica*
Photograph				
Material size (mm)	Length < 30	Length < 30	15 × 10 × 5	15 × 10 × 5
Fiber analysis (wt.%)[*]				
Hemicellulose	34.00	12.50	15.35	16.01
Cellulose	26.78	47.10	48.36	43.60
Lignin	16.08	31.35	21.26	32.20
Other	23.14	9.05	15.03	8.19
Proximate analysis (wt.%)[*]				
Volatile matter (VM)	72.46	75.64	81.07	80.82
Fixed carbon (FC)	20.51	23.72	18.93	19.18
Ash	7.03	0.64	0.00	0.00
Elemental analysis (wt.%)[**]				
C	51.94	51.77	50.77	51.73
H	4.75	4.43	5.13	5.30
O[***]	40.60	42.87	44.10	42.80
N	2.43	0.93	0.00	0.17
S	0.28	0.00	0.00	0.00
HHV (MJ kg^{-1})[*]	17.13	18.25	18.38	18.59

[*] Dry basis, 0% = ND.
[**] Dry-ash-free.
[***] By difference, O (wt.%) = 100–C–H–N–S.

lowest HHV (=17.13 MJ kg^{-1}) among the four samples. OPF and CF were trimmed and meshed to the lengths less than 30 mm where needle-shaped materials were obtained. EU and CJ were cut into blocks with the dimensions of 15 × 10 × 5 mm. The samples were dried in an oven at 105 °C until the moisture content was zero. The moisture content was measured by means of a moisture analyzer (Ohaus MB45).

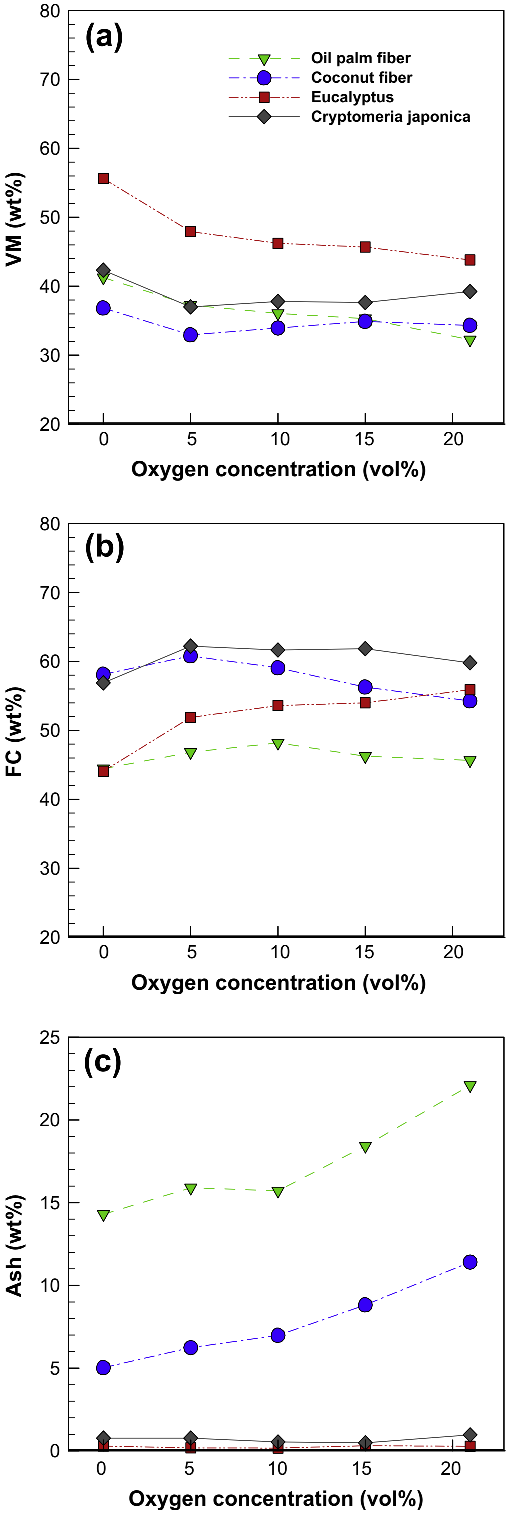

Fig. 1. (a) VM (b) FC and (c) ash of inertly and oxidatively torrefied biomasses in various oxygen concentrations.

2.2. Torrefaction and sample analysis

The torrefaction system was made up of a reactor, a gas supply unit, a product gas treatment unit, and a cooling unit. Detailed description of the system can be found elsewhere [13]. In the experiments of biomass pretreatment, the weights of fibrous biomass and ligneous biomass were fixed at 10 g (±5%) and 20 g (±5%), respectively, as a consequence of different densities. It was described in the introduction that the torrefaction temperatures of 280 °C had a slight impact on the oxidative torrefaction of eucalyptus, except at the O_2 concentration of 21 vol.% [26]. Meanwhile, when the torrefaction temperature was higher than or equal to 325 °C, the ash content of the pretreated oil palm fiber with oxidative torrefaction was high, and the HHV of the biomass was reduced in a significant way [28]. Therefore, the samples were torrefied at 300 °C for 1 h and the volumetric flow rate of carrier gas was 1000 mL min^{-1} (25 °C). After the carrier gas left the reactor, it was cooled and washed in conical flasks. The solid residues were cooled to room temperature in the cooling unit for further analysis. Five different oxygen concentrations of 0, 5, 10, 15, and 21 vol.% in the carrier gas were considered to evaluate the influence of oxygen concentration on the performance of torrefaction. The oxygen concentration in the carrier gas was controlled by mixing nitrogen and air at different flow rates, and the two gases were individually controlled by two mass flow controllers (Alicat Scientific). Prior to carrying out experiments, the mass flow controllers were calibrated by a flow calibrator (mini-Buck Calibrator M-30) to ensure the quality of oxygen concentration of the carrier gas. After the samples experienced torrefaction, the proximate (ASTM E870-82), elemental (Vario EL III), fiber, and calorific (IKA C2000 Basic) analyses of the raw biomass and torrefied materials were carried out. The microstructures of all the samples were examined using two scanning electron microscopes (SEMs). Raw and torr-

Table 2
A list of the elemental analyses of raw and torrefied biomasses.

Biomass	O_2 conc. (vol.%)	Elemental analysis* (wt.%)				
		C	H	O**	N	S
Oil palm fiber						
	Untreated	51.94	4.75	40.60	2.43	0.28
	0	70.07	4.90	23.20	1.65	0.18
	5	68.07	2.98	26.44	2.51	0.00
	10	69.14	2.39	26.09	2.38	0.00
	15	66.60	2.41	27.88	3.11	0.00
	21	68.28	2.61	25.84	3.27	0.00
Coconut fiber						
	Untreated	51.77	4.43	42.87	0.93	0.00
	0	72.45	3.92	22.97	0.66	0.00
	5	76.07	2.69	20.92	0.32	0.00
	10	74.29	2.22	23.12	0.37	0.00
	15	73.48	1.78	24.30	0.44	0.00
	21	71.58	1.66	26.08	0.68	0.00
Eucalyptus						
	Untreated	50.77	5.13	44.10	0.00	0.00
	0	68.42	4.18	27.40	0.00	0.00
	5	68.90	3.57	27.53	0.00	0.00
	10	68.48	3.33	28.19	0.00	0.00
	15	68.18	3.05	28.77	0.00	0.00
	21	71.48	2.19	26.33	0.00	0.00
Cryptomeria japonica						
	Untreated	51.73	5.30	42.80	0.17	0.00
	0	73.30	4.35	22.35	0.00	0.00
	5	75.25	3.48	21.27	0.00	0.00
	10	74.37	2.66	22.97	0.00	0.00
	15	74.20	1.88	23.92	0.00	0.00
	21	74.09	2.25	23.66	0.00	0.00

* Dry basis ash free, 0% = ND.
** By difference, O (wt.%) = 100–C–H–N–S.

efied OPF and CF were observed by a high-powered SEM (Zeiss AURIGA), and untreated and treated EU and CJ were observed via a low-powered SEM (JEOL, JSM-630). To ascertain the experimental quality, the experiment under any given condition was usually carried out more than twice. In this work, relative differences among the measurements were controlled below 5%.

3. Results and discussion

3.1. Proximate and elemental analyses

Volatile matter (VM) and fixed carbon (FC) are two important indexes of solid fuels. A higher VM in a material gives a more reactive fuel along with less calorific value, whereas a high FC material means that the fuel is less reactive but its calorific value is high. Fig. 1a suggests that the VM of OPF and EU decreases monotonically with increasing O_2 concentration, but the VM of CF and CJ is relative insensitive to the change of O_2 concentration. The decline in the VM of EU is relatively pronounced; this is the reason why its FC increases when the O_2 concentration rises, as shown in Fig. 1b. The VM of untreated EU is close to that of raw CJ (Table 1). The lower VM in torrefied CJ than in torrefied EU (Fig. 1a) reveals that it is easier for the former to liberate light hydrocarbons in the course of non-oxidative and oxidative torrefaction. The inconsistent distributions in VM and FC (Fig. 1a and b) reflect the fact that the type of biomass plays an important role in determining the results of oxidative torrefaction. In examining the ash contents of the samples, Fig. 1c depicts that the ash contents of OPF and CF are substantially lifted when the O_2 concentration increases. This is attributed to the needle shape of OPF and CF which has a larger surface area, rendering the two biomasses to react with oxygen more easily. In contrast, the ash contents of EU and CJ were very low (less than 1 wt.%), even though they were torrefied in oxidative environments.

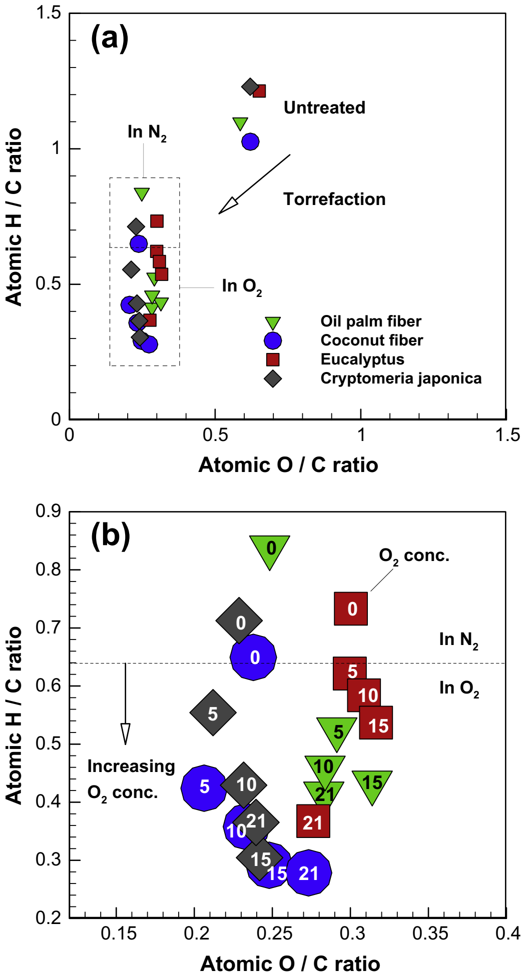

Fig. 2. (a) Over view (b) inertly and oxidatively torrefaction area of atomic H/C versus O/C of biomasses in various oxygen concentrations.

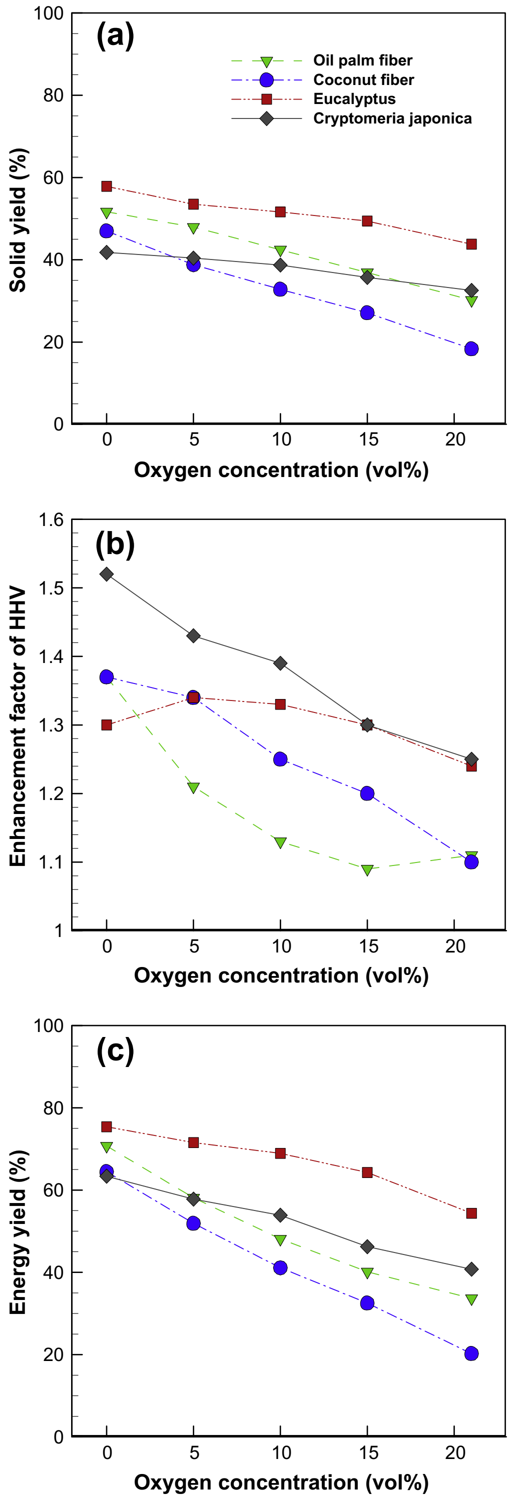

Fig. 3. (a) Solid yield (b) HHV increased and (c) energy yield of inertly and oxidatively torrefied biomasses in various oxygen concentrations.

Table 3
A list of HHVs of untreated and torrefied biomasses from measurements and predictions and their comparison.

Biomass	O_2 conc. (vol.%)	Measurement	Prediction based on Eq. (1)		Prediction based on Eq. (2)	
		HHV (MJ kg^{-1})	HHV (MJ kg^{-1})	Relative error (%)	HHV (MJ kg^{-1})	Relative error (%)
Oil palm fiber						
	Untreated	17.13	17.97	4.90	18.97	10.75
	0	23.45	21.61	7.83	19.06	18.69
	5	20.77	19.44	6.39	18.91	8.96
	10	19.43	19.32	0.55	19.02	2.07
	15	18.63	18.26	1.99	18.39	1.31
	21	19.09	18.22	4.56	17.66	7.53
Coconut fiber						
	Untreated	18.25	18.80	2.99	20.39	11.69
	0	25.04	23.42	6.46	21.67	13.44
	5	24.41	23.21	4.93	21.61	11.48
	10	22.86	22.19	2.94	21.36	6.57
	15	21.90	21.26	2.89	20.84	4.85
	21	20.14	20.18	0.19	20.22	0.40
Eucalyptus						
	Untreated	18.38	19.20	4.48	20.22	9.99
	0	23.95	23.56	1.62	21.71	9.35
	5	24.58	23.22	5.52	22.21	9.62
	10	24.53	22.91	6.64	22.32	9.03
	15	23.91	22.55	5.66	22.32	6.65
	21	22.82	22.82	0.00	22.44	1.66
Cryptomeria japonica						
	Untreated	18.59	19.63	5.59	20.23	8.83
	0	28.18	25.02	11.22	22.41	20.48
	5	26.59	24.87	6.46	22.74	14.48
	10	25.87	24.00	7.24	22.75	12.09
	15	24.07	23.32	3.14	22.77	5.43
	21	23.28	23.48	0.86	22.55	3.13

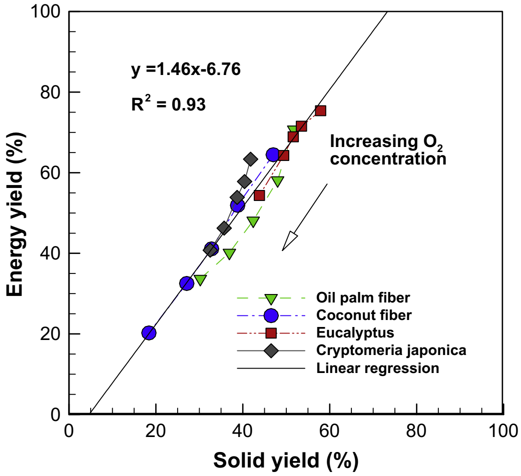

Fig. 5. Distribution of energy yield of torrefied biomass.

The weight percentages of elements C, H, O, N, and S of the raw and torrefied samples are given in Table 2. Whether the biomass is torrefied in N_2 or O_2, the elements H and O in the raw biomass are reduced markedly, whereas the element C is increased. It is known that torrefaction belongs to a mild pyrolysis process. Therefore, relatively more carbon is retained in torrefied biomass than hydrogen and oxygen when compared to raw biomass. This is a result of carbonization reaction and this is the reason why altering O_2 concentration merely has a slight influence on carbon content. With regard to element hydrogen, Table 2 indicates that hydrogen in torrefied biomass has a trend to decrease with increasing O_2 concentration, except for oil palm fiber whose hydrogen is relatively insensitive to O_2 concentration when its value is no less than 10 vol.%. This reveals that it is easier for oxygen in the carrier gas to react with hydrogen than with carbon. A comparison to the biomass torrefied in N_2, it is noteworthy that element O in the biomass has a trend to grow when the O_2 concentration increases. Fang et al. [29] mentioned that the mass loss rates of wood in a thermogravimetric analyzer at different oxygen concentrations were similar to each other when the temperature was below 250 °C. Rousset et al. [16] pointed out that different O_2 concentrations did not significantly affect the composition of solid residue at 240 °C. The van Kelvelen diagram shown in Fig. 2a indicates that both the atomic H/C and O/C ratios drop notably once the samples are torrefied, especially for the atomic H/C ratio. If the diagram is examined in more detail, the atomic H/C and O/C ratios shown in Fig. 2b are in the ranges of approximately 0.2–0.9 and 0.2–0.35, respectively. This suggests that varying O_2 concentration has a pronounced influence on the atomic H/C ratio, whereas the atomic O/C ratio is fairly insensitive to the O_2 concentration. The obtained results differ from those of Fang et al. [29] and Rousset et al. [16] mainly due to the torrefaction operated at 300 °C in the current study. In a non-oxidative torrefaction environment, the devolatilization and pyrolysis of biomass are the prime mechanisms of thermal degradation. The release of moisture and light volatiles and the depletion of hemicellulose result in the linear profile between the atomic H/C ratio and the atomic O/C ratio in a

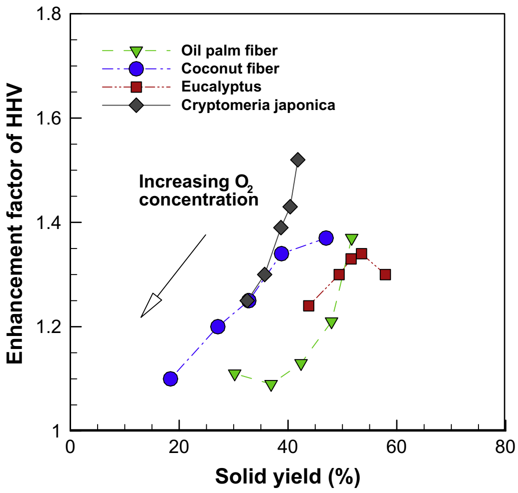

Fig. 4. Distribution of enhancement factor of HHV of torrefied biomass.

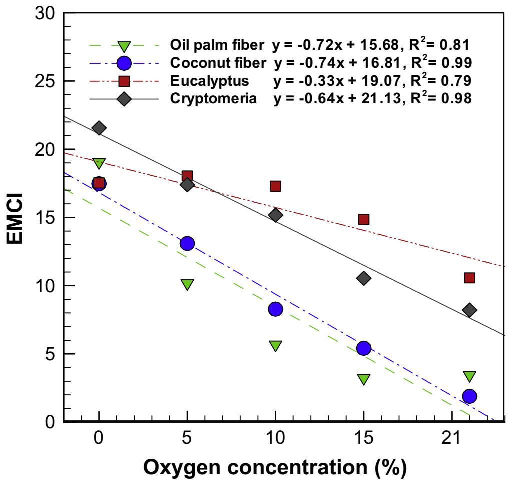

Fig. 6. Distribution of EMCI of torrefied biomass.

van Kelvelen diagram [6]. In an oxidative environment, the oxidation of hydrocarbons also plays a virtual role in decomposing biomass [30,31]. In view of oxygen supplied externally and the carbonization of biomass where in the former relatively more hydrogen and less internal oxygen in biomass are consumed (Table 2), this leads to a decrease in the atomic H/C ratio as the O_2 concentration increases. In contrast, the impact of O_2 concentration on atomic O/C ratio is slight.

3.2. Solid and energy yields

The solid yield is an indicator of how biomass resists to thermal degradation and it is defined as

$$\text{Solid yield}(\%) = \frac{\text{Weight of pretreated biomass}}{\text{Weight of raw biomass}} \times 100 \qquad (1)$$

In observing the profiles of solid yield shown in Fig. 3a, an increase in O_2 concentration lowers the solid yield, regardless of which biomass is. EU possesses the highest solid yields among the four samples, indicating its higher resistance against thermal degradation. The decreasing trend in the solid yield of OPF and CF with increasing O_2 concentration is deeper than those of the other two species. This can be explained by their smaller sizes and higher surface areas. Fig. 3b depicts that the enhancement factor of HHV (=HHV of pretreated biomass/HHV of raw biomass) of the four materials within the investigated range of O_2 concentration is between 1.30 and 1.52. The energy yield is defined as

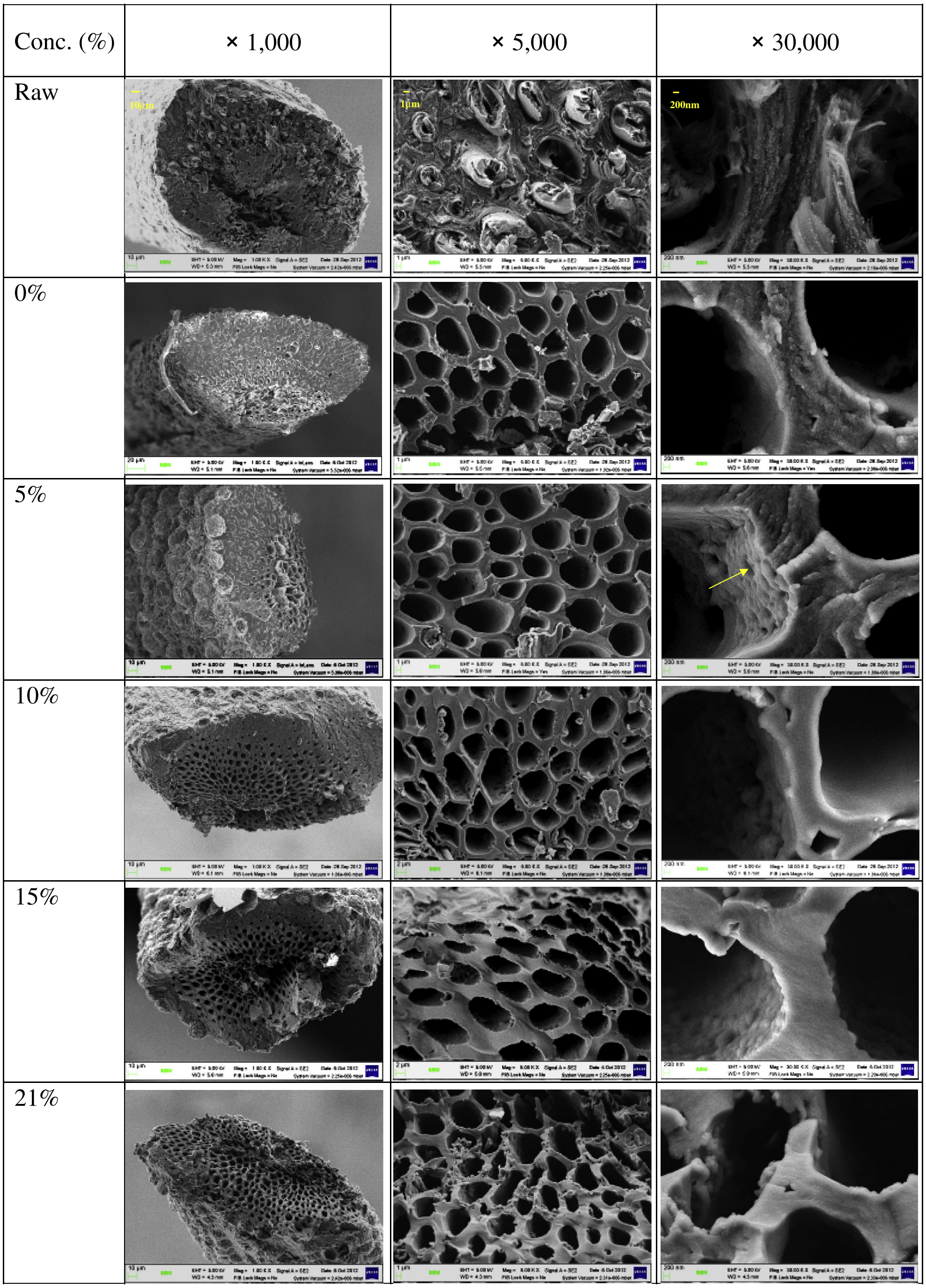

Fig. 7. SEM images of untreated, inertly and oxidatively torrefied oil palm fiber.

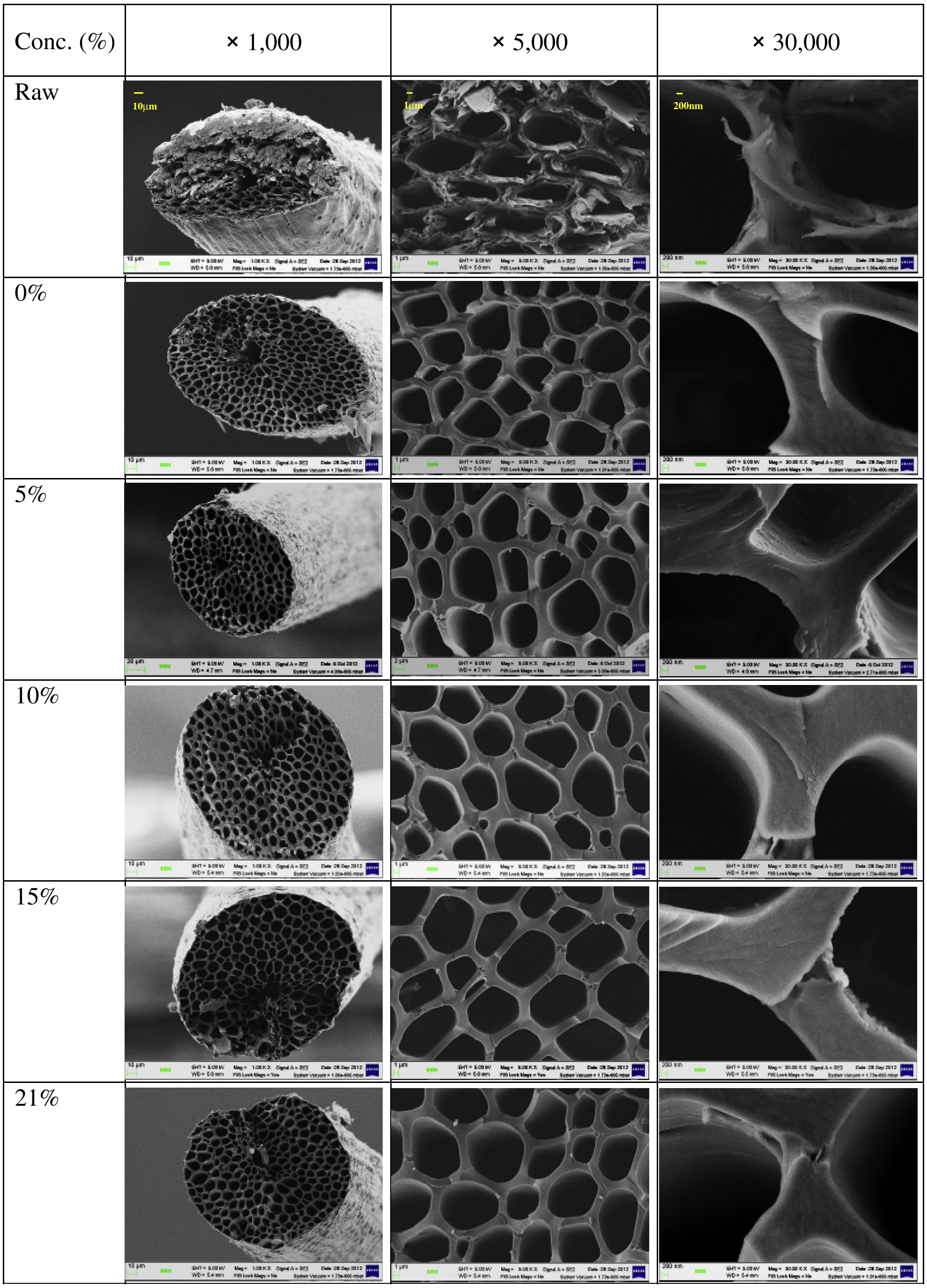

Fig. 8. SEM images of untreated, inertly and oxidatively torrefied coconut fiber.

$$\text{Energy yield}(\%) = \frac{\text{HHV}_{\text{pretreated biomass}} \times \text{weight of pretreated biomass}}{\text{HHV}_{\text{raw biomass}} \times \text{weight of raw biomass}} \times 100 \quad (2)$$

This definition is equivalent to solid yield × enhancement factor of HHV. Fig. 3c shows the profiles of the energy yield of the four species. Similar to the profiles in Fig. 3a, OPF and CF have a deeper decay in energy yield. It follows that the role played by the solid yield on energy yield prevails over that played by the enhancement factor. The energy yield of EU is the highest among the four materials, ranging from 54.4% to 75.4%. This implies that EU is the most suitable species for both non-oxidative and oxidative torrefaction. The energy yield of CF is around 20.2% from its torrefaction at the O_2 concentration of 21 vol.%. Accordingly, it is inappropriate for CF to be torrefied in air.

3.3. Prediction of HHV and operating index

HHV is a primary property of biomass as a fuel. Channiwala and Parikh [32] developed an empirical correlation based on elemental and proximate analyses to predict the HHV of raw biomass. Yin [33] also developed two simple correlations individually in terms of elemental and proximate analyses to predict the HHV of raw biomass. The correlations are expressed as follows

$$\text{HHV (MJ kg}^{-1}) = 0.2949\ \text{C} + 0.8250\ \text{H (dry basis)} \quad (3)$$

$$\text{HHV(MJ kg}^{-1}) = 0.1905\ \text{VM} + 0.2521\ \text{FC(dry basis)} \quad (4)$$

The measured and predicted HHVs in accordance with the preceding equations are tabulated in Table 3 and compared with each other. The predicted results are in good agreement with the

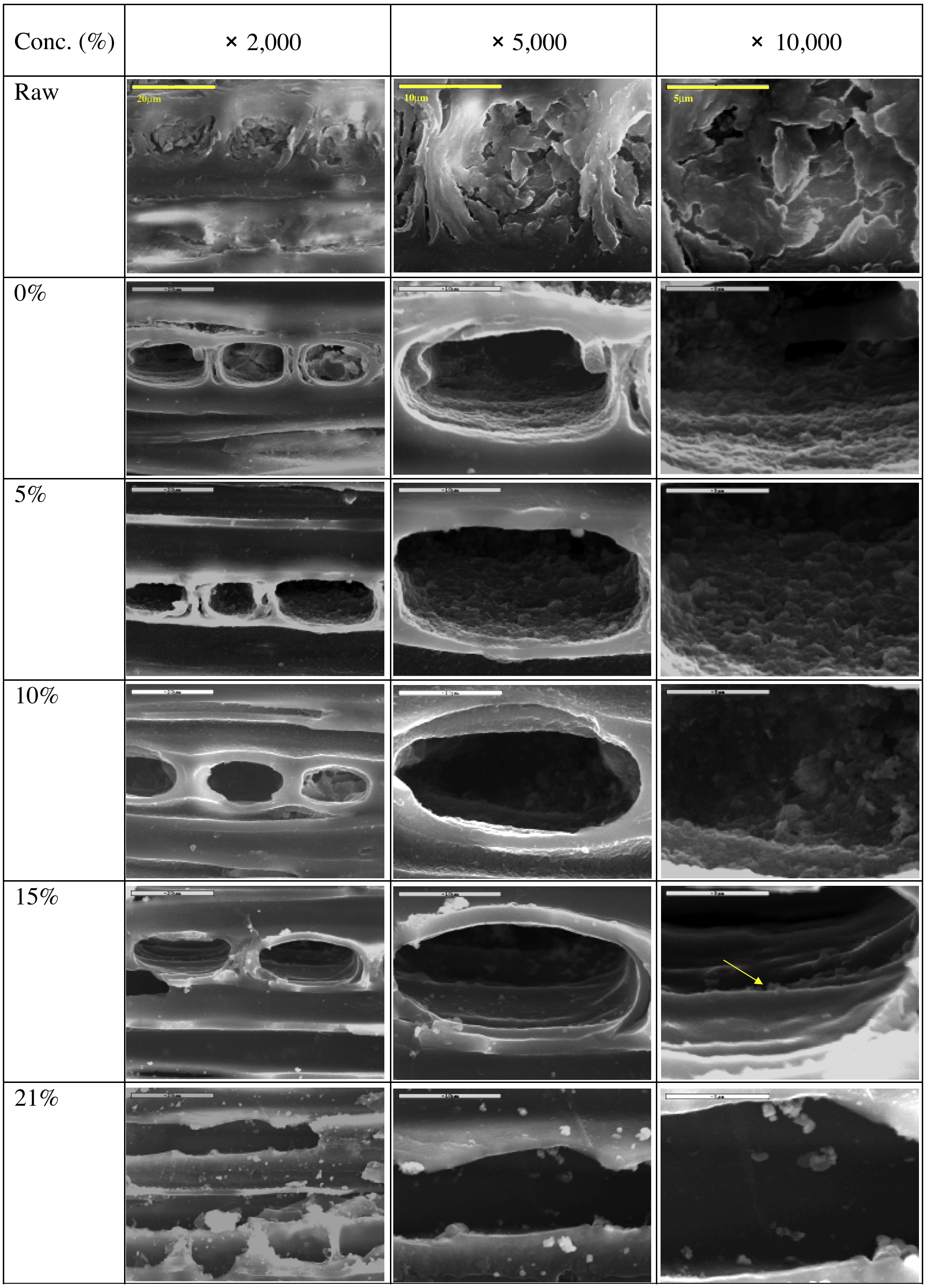

Fig. 9. SEM images of untreated, inertly and oxidatively torrefied eucalyptus.

measured ones in that most of the relative errors are below 10%. Overall, Eq. (3) gives better predictions than Eq. (4), even though element oxygen is not taken into account in the former. Consequently, the two empirical correlations for raw biomass can also be used to predict the HHVs of torrefied biomass under non-oxidative and oxidative torrefaction, especially for Eq. (3).

For non-oxidative torrefaction, an increase in torrefaction temperature or duration reduces the solid yield, but it is usually accompanied by an increase in the calorific value of a material. The study of Almeida et al. [34] indicated that the calorific value of a material is linearly proportional to the mass loss, implying that a decrease in solid yield increases the calorific value of biomass. Upon inspection of the plot of enhancement factor of HHV versus solid yield under oxidative torrefaction shown in Fig. 4, it is of interest that an opposite trend to non-oxidative torrefaction is exhibited. That is, an increase in solid yield enlarges the enhancement factor. The correlation of energy yield and solid yield shown in Fig. 5 is characterized by a strongly linear relationship ($R^2 = 0.93$). In the study of Lu et al. [13] a parameter of energy-mass co-benefit index, EMCI (=energy yield – solid yield), for torrefaction operation was introduced. A higher EMCI stands for torrefied biomass being featured by a higher energy density and a lower volume. Fig. 6 suggests that non-oxidative torrefaction always gives the highest EMCI, regardless of which biomass is torrefied. The value of EMCI declines linearly with increasing O_2 concentration. This implies, in turn, that a carrier gas with higher O_2 concentration deteriorates the performance of torrefaction. The slope of the regression line represents the sensitivity of a tested

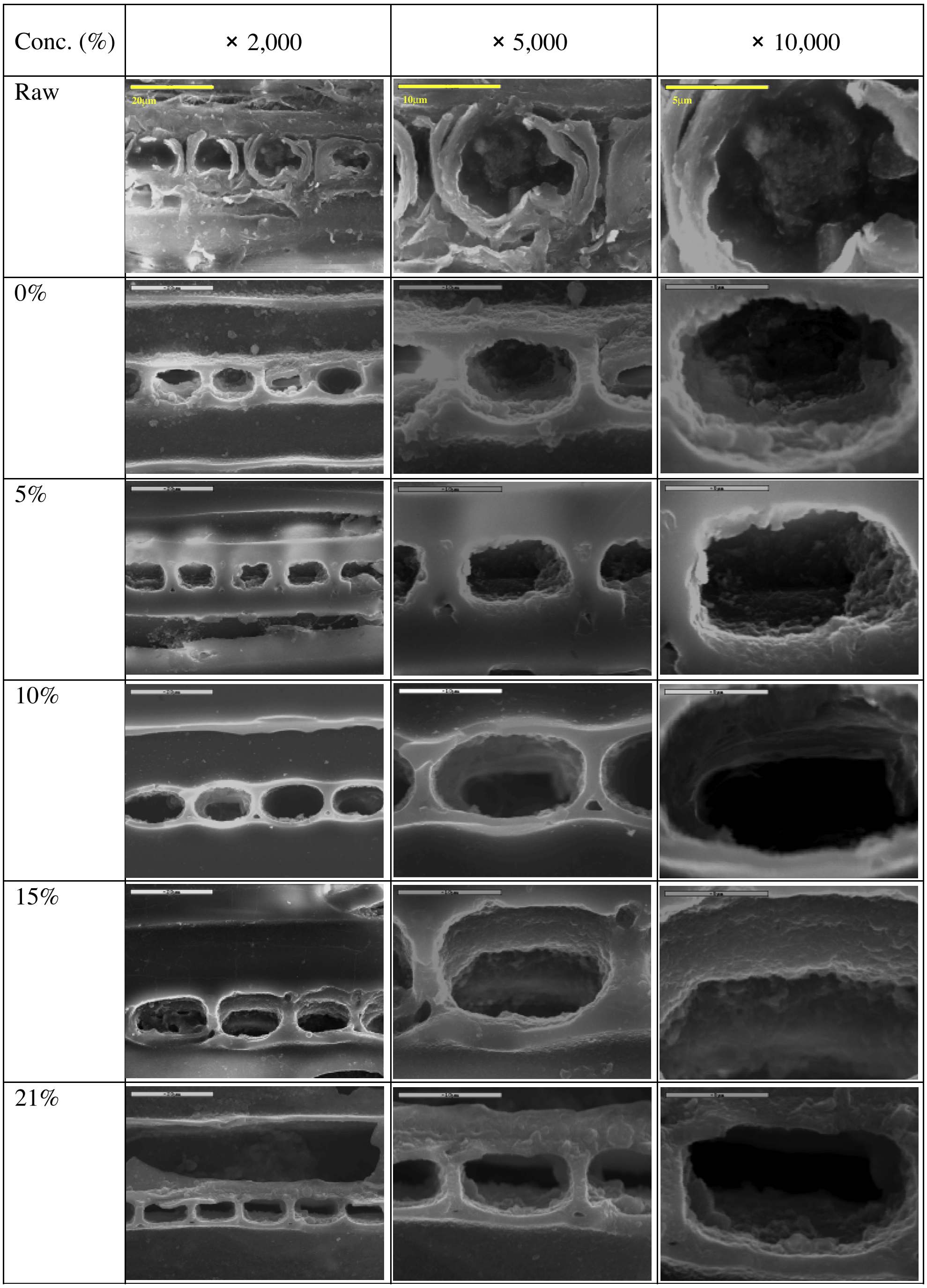

Fig. 10. SEM images of untreated, inertly and oxidatively torrefied *Cryptomeria japonica*.

material to oxidative torrefaction under altered O_2 concentration. EU has the highest resistance to oxidative torrefaction in that it has the largest slope, as observed in Fig. 3. It is thus recognized that though oxidative torrefaction is able to reduce the operating cost of a torrefaction process, it also diminishes the performance of the process. How to find an optimum operation for balancing the cost and the performance of torrefaction significantly depends on the nature of biomass and it deserves further investigation in the future.

3.4. SEM observation

To gain a deeper insight into the impact of non-oxidative and oxidative torrefaction on biomass structure, the SEM images of OPF and CF before and after torrefaction are shown in Figs. 7 and 8, respectively. The images are amplified by factors of 1 K, 5 K, and 30 K to demonstrate the microstructures of biomass cross sections. There are plentiful inclusions in the thick-walled fibers of raw OPF and CF (×5 K), especially for the former. After undergoing non-oxidative torrefaction, a lot of inclusions disappear and the tubular structure is clearly exhibited. This is mainly owing to the depletion of hemicellulose and a small part of lignin. This variation in microstructure can explain why the grindability of torrefied biomass is better than that of its parent biomass [35]. Following the torrefaction at the O_2 concentration of 5 vol.%, the thick-walled fibers of OPF are damaged so that a number of tiny holes are observed on the fibers (Fig. 7, ×30 K, indicated by arrow). This is attributed to the lignocellulosic oxidation in biomass. When the

O_2 concentration rises, the tubular structure becomes more significant (×1 K). Once the O_2 concentration is as high as 21 vol.%, the tubular structure is even destroyed to a certain extent (×30 K). With regard to CF, increasing O_2 concentration seems to have less impact on its microstructure (Fig. 8). This may be due to the higher lignin content in CF (Table 2) which has a higher resistance against thermal oxidation.

The cross section images of EU and CJ are displayed in Figs. 9 and 10, respectively, where they are amplified by factors of 2 K, 5 K, and 10 K. It is apparent that the internal structures of the two materials (Figs. 9 and 10) are different from those of OPF and CF (Figs. 7 and 8). The cells in raw EU and CJ are also filled with inclusions. When they are torrefied in N_2, the inclusions are consumed drastically and the cell structures are clearly exhibited (×2 K). Basically, when oxidative torrefaction is carried out, its impact on the cell structure is similar to that of non-oxidative torrefaction. This reveals that the internal structure of the ligneous biomass is relatively insensitive to the oxidative reaction in a torrefaction environment. In other words, the ligneous biomass has a higher resistance against oxidation torrefaction than the fibrous biomass. This is the reason that altering O_2 concentration has a smaller influence on the energy yields of EU and CJ when compared to OPF and CF (Fig. 3c). At the O_2 concentration of 15 vol.%, the interior of the cell of EU becomes smoother (Fig. 9, ×10 K, indicated by arrow), and the cell structure of EU is even destroyed to a certain extent at the O_2 concentration of 21 vol.% (Fig. 9, ×2 K). Though the cell in CJ is retained from the oxidative torrefaction at the O_2 concentration of 21 vol.%, the cell walls become thinner (Fig. 10, ×5 K).

4. Conclusions

Four different types of biomass (i.e. oil palm fiber, coconut fiber, eucalyptus, and *Cryptomeria japonica*) torrefied at 300 °C for 1 h in non-oxidative and oxidative environments have been investigated and compared with each other. The results suggest that the non-oxidative torrefaction always gives the highest energy-mass co-benefit index (EMCI), regardless of which biomass is torrefied; that is, the performance of biomass torrefied in N_2 is higher than in an oxidative atmosphere. The distributions of EMCI indicate that oil palm fiber and coconut fiber are more sensitive to oxygen concentration, whereas eucalyptus has the least sensitivity to the concentration. In the environment of oxidative torrefaction, an increase in O_2 concentration deteriorates the torrefaction performance. A linear relationship between the solid yield and the calorific value is exhibited in oxidative torrefaction. Contrary to the behavior of non-oxidative torrefaction, decreasing solid yield leads to the decrease of energy yield. SEM observations indicate that ligneous biomass has higher resistance against oxidation torrefaction than fibrous biomass, so the former is more suitable for oxidative torrefaction than the latter. In other words, ligneous biomass can be torrefied in oxidative environments at low oxygen concentrations to reduce the operating cost of biomass pretreatment.

Acknowledgments

The authors gratefully acknowledge the financial support of China Steel Corporation, Taiwan, ROC, for this study.

References

[1] International Energy Agency. World Energy Outlook; 2011.
[2] Sami M, Annamalai K, Wooldridge M. Co-firing of coal and biomass fuel blends. Prog Energy Combust Sci 2001;27:171–214.
[3] McLendon TR, Lui AP, Pineault RL, Beer SK, Richardson SW. High-pressure co-gasification of coal and biomass in a fluidized bed. Biomass Bioenerg 2004;6:377–88.
[4] Chen WH, Wu JS. An evaluation on rice husks and pulverized coal blends using a drop tube furnace and a thermogravimetric analyzer for application to a blast furnace. Energy 2009;34:1458–66.
[5] Idris SS, Rahman NA, Ismail K, Alias AB, Rashid ZA, Aris MJ. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). Bioresour Technol 2010;101:4584–92.
[6] Chew JJ, Doshi V. Recent advances in biomass pretreatment-torrefaction fundamentals and technology. Renew Sust Energy Rev 2011;15:4212–22.
[7] Parikh J, Channiwala SA, Ghosal GK. A correlation for calculating HHV from proximate analysis of solid fuels. Fuel 2005;84:487–90.
[8] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour Technol 2011;102:1246–53.
[9] Tapasvi D, Khalil R, Skreiberg Ø, Tran KQ, Grønli M. Torrefaction of Norwegian birch and spruce: an experimental study using macro-TGA. Energy Fuels 2012;26:5232–40.
[10] Chen WH, Kuo PC. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. Energy 2011;36:6451–60.
[11] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 2008;87:844–56.
[12] Wannapeera J, Fungtammasan B, Worasuwannarak N. Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass. J Anal Appl Pyrol 2011;92:99–105.
[13] Lu KM, Lee WJ, Chen WH, Liu SH, Lin TC. Torrefaction and low temperature carbonization of oil palm fiber and eucalyptus in nitrogen and air atmospheres. Bioresour Technol 2012;123:98–105.
[14] Chen WH, Du SW, Tsai CH, Wang ZY. Torrefied biomasses in a drop tube furnace to evaluate their utility in blast furnaces. Bioresour Technol 2012;111:433–8.
[15] Chen Q, Zhou JS, Liu BJ, Mei QF, Luo ZY. Influence of torrefaction pretreatment on biomass gasification technology. Chinese Sci Bull 2011;56:1449–56.
[16] Rousset P, Aguiar C, Labbe N, Commandre JM. Enhancing the combustible properties of bamboo by torrefaction. Bioresour Technol 2011;102:8225–31.
[17] Peng JH, Bi HT, Sokhansanj S, Lim JC. A study of particle size effect on biomass torrefaction and densification. Energy Fuels 2012;26:3826–39.
[18] Chen WH, Hsu HC, Lu KM, Lee WJ, Lin TC. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. Energy 2011;36:3012–21.
[19] Uemura Y, Omar WN, Tsutsui T, Yusup SB. Torrefaction of oil palm wastes. Fuel 2011;90:2585–91.
[20] Li H, Liu X, Legros R, Bi XT, Lim CJ, Sokhansanj S. Torrefaction of sawdust in a fluidized bed reactor. Bioresour Technol 2012;103:453–8.
[21] Lee JW, Kim YH, Lee SM, Lee HW. Optimizing the torrefaction of mixed softwood by response surface methodology for biomass upgrading to high energy density. Bioresour Technol 2012;116:471–6.
[22] Deng J, Wang GJ, Kuang JH, Zhang YL, Luo YH. Pretreatment of agricultural residues for co-gasification via torrefaction. J Anal Appl Pyrol 2009;86:331–7.
[23] Chen WH, Lu KM, Tsai CM. An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. Appl Energy 2012;100:318–25.
[24] Meng J, Park J, Tilotta D, Park S. The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil. Bioresour Technol 2012;111:439–46.
[25] Wang C, Peng J, Li H, Bi XT, Legros R, Lim CJ, et al. Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. Bioresour Technol 2013;127:318–25.
[26] Rousset P, Macedo L, Commandré JM, Moreira A. Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. J Anal Appl Pyrol 2012;96:86–91.
[27] Uemura Y, Omar W, Othman NA, Yusup S, Tsutsui T. Torrefaction of oil palm EFB in the presence of oxygen. Fuel 2013;103:156–60.
[28] Chen WH, Lu KM, Liu SH, Tsai CM, Lee WJ, Lin TC. Biomass torrefaction characteristics in inert and oxidative atmospheres at various superficial velocities. Bioresour Technol 2013;146:152–60.
[29] Fang MX, She DK, Li YX, Yu CJ, Luo ZY, Cen KF. Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG-FTIR analysis. J Anal Appl Pyrol 2006;77:22–7.
[30] Munir S, Daood SS, Nimmo W, Cunliffe AM, Gibbs BM. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. Bioresour Technol 2009;100:1413–8.
[31] Wongsiriamnuay T, Tippayawong N. Thermogravimetric analysis of giant sensitive plants under air atmosphere. Bioresour Technol 2010;101:9314–20.
[32] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051–63.
[33] Yin CY. Prediction of higher heating values of biomass from proximate and ultimate analyses. Fuel 2011;90:1128–32.
[34] Almeida G, Brito JO, Perre P. Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: the potential of mass loss as a synthetic indicator. Bioresour Technol 2010;101:9778–84.
[35] Chen WH, Cheng WY, Lu KM, Huang YP. An evaluation on improvement of pulverized biomass property for solid fuel through torrefaction. Appl Energy 2011;88:3636–44.